Luminescent Response to the Phase Composition of Nd^{3+}:Y_2O_3-Al_2O_3 System

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Abstract. The work demonstrates the luminescent method of identifying the phase composition of Nd^{3+}:Y_2O_3-Al_2O_3 system by building calibration curves using standard samples.

1. Introduction

The most prominent problem in the synthesis of optical ceramics is the one of controlling the presence of impurity phases, as even in small amounts they impact the optical properties severely [1]. The presence of a large amount of structural modifications and polymorphic changes in the process of ceramics synthesis requires the use of rapid and sensitive analytic methods for synthesis technology correction and final ceramics quality inspection. The standard method of phase composition identification is X-ray phase analysis. Meanwhile, it is the luminescent method that is a rapid and qualitatively more sensitive one for phase composition identification [2,3]. In paper [2], the luminescent method was used for quantitative phase analysis of Nd^{3+}:YAG (yttrium-aluminium garnet Nd^{3+}:$Y_3Al_5O_{12}$) ceramics and monocrystals with Nd^{3+}:YAP (yttrium-aluminium perovskite Nd^{3+}:$YAlO_3$) impurity phase. Physically, the method is based on different locations of Stark emission bands of Nd^{3+} ion in crystal fields of various structures [4]. The luminescent parameter determining the concentration of the impurity phase is the ratio of light sums taken from two different spectrum ranges that include Nd^{3+} ion emission bands localized both in YAG and YAP structures.

The purpose of this paper is to identify the quantitative phase composition using the luminescent method for Nd^{3+}:Y_2O_3-Al_2O_3 system.

2. Objects of research and experimental equipment

Specially prepared multiphase Nd^{3+}:Y_2O_3-Al_2O_3 systems used as the objects of the research. The starting material used were nanopowders of monoclinic Al_2O_3 and Nd^{3+}:Y_2O_3 prepared with the

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method of target laser evaporation with a repetitively pulsed CO_2 LAERT laser, the mean emission power of which is 500 W and the emission wavelength is 10.6 μm [5]. Used as targets were commercial Al_2O_3 micron powder and a mixture of Y_2O_3 microsized powder and 1 mol. % of Nd_2O_3 powders, respectively. The resulting Nd^{3+}:Y_2O_3 and Al_2O_3 nanopowders were annealed at 1000 °C during 30 min and at 1250 °C during 3 h, respectively. Then, Nd^{3+}:Y_2O_3 and Al_2O_3 nanopowders were blended, with the ratio (Nd + Y) : Al = 3 : 5, which corresponds to yttrium-aluminium garnet stoichiometry. To prepare a multiphase system, a certain excessive amount of yttrium oxide or aluminium oxide was added to the resulting mixtures. The blending was carried out in ethanol during 48 h. After drying, the nanopowder mixtures were pressed into compacts with the method of dry monoaxial static pressing at 200 mPa. The prepared compact was annealed at 800 °C during 3 h, with following sintering at 1780°C during 20 h. The ceramics obtained was additionally annealed at 1300 °C for 5 h to reach transparency.

The additionally used one-phase samples were a Nd^{3+}:YAP monocrystal, monoclinic Al_2O_3 and cubic Nd^{3+}:Y_2O_3 nanopowders. The latter was obtained by annealing the starting monoclinic nanopowder in the air at T = 1500 °C during 3 h.

Photoluminescence (PL) was excited by DMH 808-4000 laser diode, emission wavelength 808 nm, emission power 4W. A spectrograph photodetector was represented by Hamamatsu G9214-512S semiconductor InGaAs line that included 512 elements with the discretion of 0.5 nm at one unit of the array. The detection was carried out in the range 890-1150 nm in the air at room temperature. Pulsed cathodoluminescence (PCL) was excited by an electronic beam with the mean energy 180 keV and pulse duration of 2 ns which was emitted by RADAN-220 high-current electron accelerator [3]. The spectograph photodetector contains 2,048 elements with the discretion of 0.2 nm per one unit of the line. The detection was carried out in the range 350-890 nm in the air at room temperature. Precision for wavelength identification did not exceed 0.5 nm.

The X-ray phase analysis was performed at D8 Discover diffractometer in copper emission with a graphite monochromator at a diffracted beam and also at XPert PRO MRD Panalitical diffractometer.

3. The results and discussion

Table 1 presents the tested samples and their phase composition according to the X-ray phase analysis.

Table 1. X-ray results for tested samples

	YAG, %	YAP, %	$Y_4Al_2O_9$, %	cubic Y_2O_3, %	monoclinic γ-Al_2O_3, %
Ceramics no. 1	56.5	25.3	1	3.6	13.6
Ceramics no. 2	48.6	37	1	3.7	12.8
Ceramics no. 3	33.4	52.7	2.5	5.6	5.8
Ceramics no. 4	39	47	1.7	4.7	7.6
Monocryst. Nd^{3+}:YAP	-	100	-	-	-
Nd^{3+}:YAG ceramics	100	-	-	-	-
Al_2O_3 nanopowder	-	-	-	-	100
Nd^{3+}:Y_2O_3 nanopowder	-	-	-	100	-

In Figure 1, PCL and PL spectra of the tested samples are presented according to Table 1. The spectra of ceramics no. 1,2 and 3,4 are qualitatively identical, so for illustrative purposes only the

spectra of the samples of ceramics no. 1 and no. 3 are given, with the concentration of YAG and YAP phases, respectively, exceeding 50 % (Table 1).

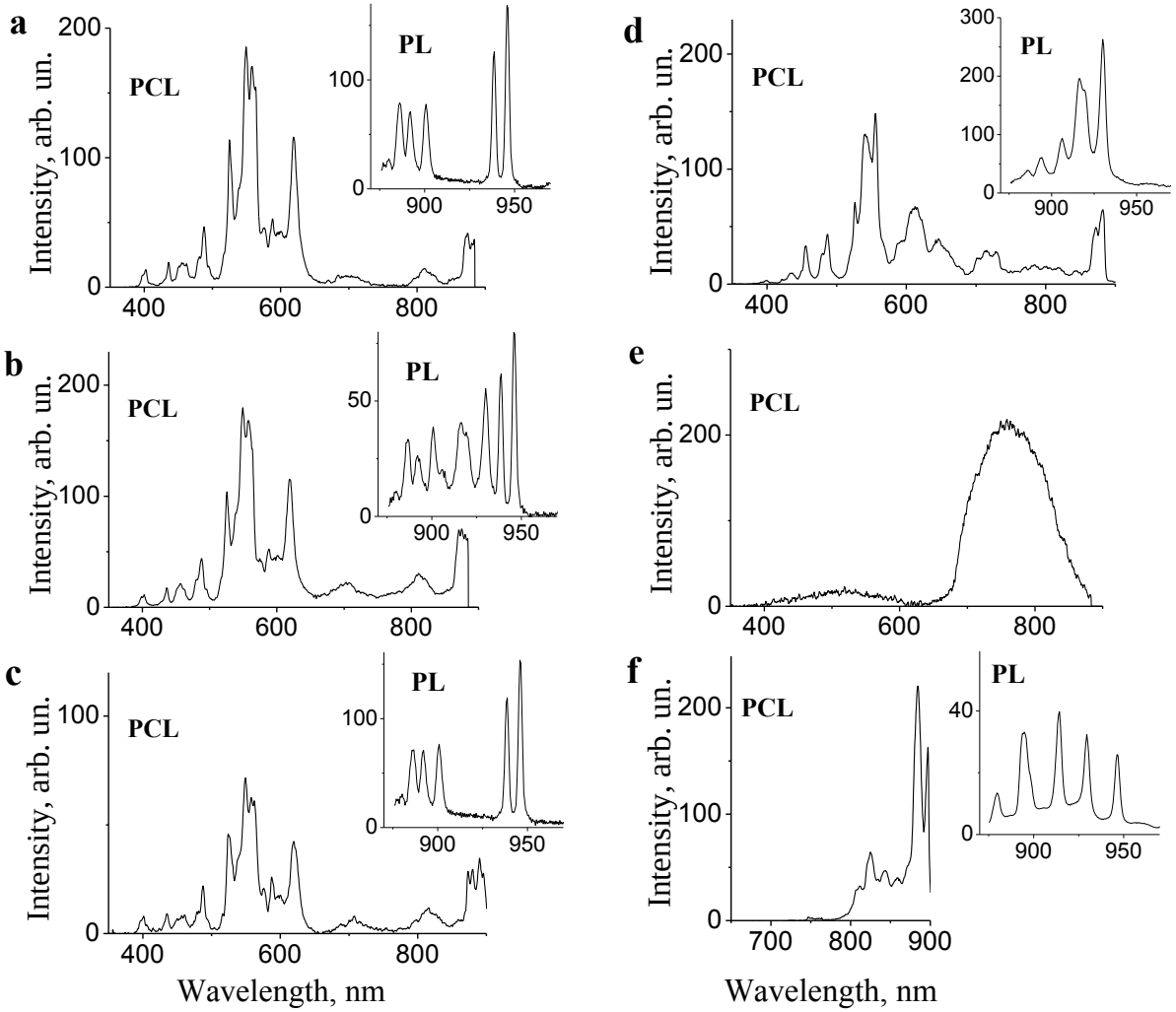

Figure 1. PCL and PL spectra: a – ceramics no. 1, b – ceramics no. 3, c – Nd^{3+}:YAG ceramics, d – Nd^{3+}:YAP monocrystal, e – monoclinic Al_2O_3 nanopowder, f - cubic Nd^{3+}:Y_2O_3 nanopowder

Assume the Nd^{3+}:YAG phase is the main one, whereas the rest of them are impurity phases. Comparative qualitative analysis of single-phase samples spectra (Fig. 1 c, d, e, f) discovered ranges where Nd^{3+}:YAG emission bands were pair-wise covered with the bands of only one of the impurity phases. That fact led to creation of a simple scheme for identifying Nd^{3+}:Y_2O_3-Al_2O_3 system phase composition with the luminescent method. It should be noted that the concentration of Nd^{3+}:$Y_4Al_2O_9$ phases was low relatively to the rest of them, which resulted in absence of any significant Nd^{3+} luminescence in $Y_4Al_2O_9$ structure in the standard samples, although the spectrum included Nd^{3+}:$Y_4Al_2O_9$ bands covered only with Nd^{3+}: YAG bands. The scheme makes it possible to determine the composition of all phases except Nd^{3+}:$Y_4Al_2O_9$.

The scheme for determination of phase composition is as follows. On the basis of the obtained pair-wise covered ranges, multiphase systems can be presented as two-phase systems:

Nd^{3+}:YAG/Nd^{3+}:YAP, Nd^{3+}:YAG/ Al_2O_3, Nd^{3+}:YAG/Nd^{3+}:Y_2O_3. In the first case the ceramics has only Nd^{3+}:YAG phases and Nd^{3+}:YAP impurity phase, in the second case it contains Nd^{3+}:YAG and Al_2O_3 impurity phase, in the third case - Nd^{3+}:YAG and Y_2O_3 impurity phase. Based on this, a recalculation of the initial percentages of phase concentrations was carried out with their ratio preserved. In Table 2 the example for the sample of ceramics no. 1 is given, where C_G, C_P, C_Y, C_A are the initial percentages of Nd^{3+}:YAG, Nd^{3+}:YAP, Nd^{3+}:Y_2O_3, Al_2O_3 concentrations according to Table 1, while $\tilde{C}_{G1}$, $\tilde{C}_{G2}$, $\tilde{C}_{G3}$, $\tilde{C}_P$, $\tilde{C}_Y$, $\tilde{C}_A$ are the recalculated concentration percentages for the three cases of two-phase systems without regard to other phases.

Table 2. Recalculation of phase concentrations for ceramics no. 1

	Ratio of initial phase concentrations	Recalculated phase concentrations ratio
Nd^{3+}:YAG/Nd^{3+}:YAP	$\frac{C_G}{C_P} = \frac{56.5}{25.3} = k_1$	$\frac{\tilde{C}_{G1}}{\tilde{C}_P} = \frac{69.071}{30.929} = k_1$
Nd^{3+}:YAG/ Al_2O_3	$\frac{C_G}{C_A} = \frac{56.5}{13.6} = k_2$	$\frac{\tilde{C}_{G2}}{\tilde{C}_A} = \frac{80.599}{19.401} = k_2$
Nd^{3+}:YAG/Nd^{3+}:Y_2O_3	$\frac{C_G}{C_Y} = \frac{56.5}{3.6} = k_3$	$\frac{\tilde{C}_{G3}}{\tilde{C}_A} = \frac{94.01}{5.99} = k_3$

For each ceramics, the following system of equations was obtained:

$$\begin{cases} \frac{C_G}{C_P} = \frac{\tilde{C}_{G1}}{\tilde{C}_P} = k_1, \\ \frac{C_G}{C_A} = \frac{\tilde{C}_{G2}}{\tilde{C}_A} = k_2, \\ \frac{C_G}{C_Y} = \frac{\tilde{C}_{G3}}{\tilde{C}_A} = k_3, \\ C_G + C_P + C_A + C_Y = 100\ \% \end{cases} \quad (1)$$

To determine concentrations of phases $\tilde{C}_{G1}$, $\tilde{C}_{G2}$, $\tilde{C}_{G3}$, $\tilde{C}_P$, $\tilde{C}_Y$, $\tilde{C}_A$ the luminescent method for two-phase systems was used [2], where the parameter determining the concentration of the impurity phase is the ratio of light sums taken from two different spectrum ranges that include emission bands only from two phases. For a system consisting only of Nd^{3+}:YAG and Nd^{3+}:YAP, the luminescent parameter was calculated the following way:

$$l_{G/P} = \frac{S_1}{S_2} = \frac{\int_{420}^{580} I(\lambda)\, d\lambda}{\int_{420}^{505} I(\lambda)\, d\lambda}, \quad (2)$$

where $I(\lambda)$ – is the luminescence intensity at wavelength λ measured in nm. After finding coefficient $l_{G/P}$ for the researched multiphase systems and for single-phase Nd^{3+}:YAG and Nd^{3+}:YAP, dependency $\tilde{C}_P(l_{G/P})$ was built (Figure 2a). With the help of approximation of the experimental points on the hyperbolic curve [2], a calibration curve was obtained, equation of which allows to find the ratio Nd^{3+}:YAG/Nd^{3+}:YAP using the luminescent method (Figure 2a).

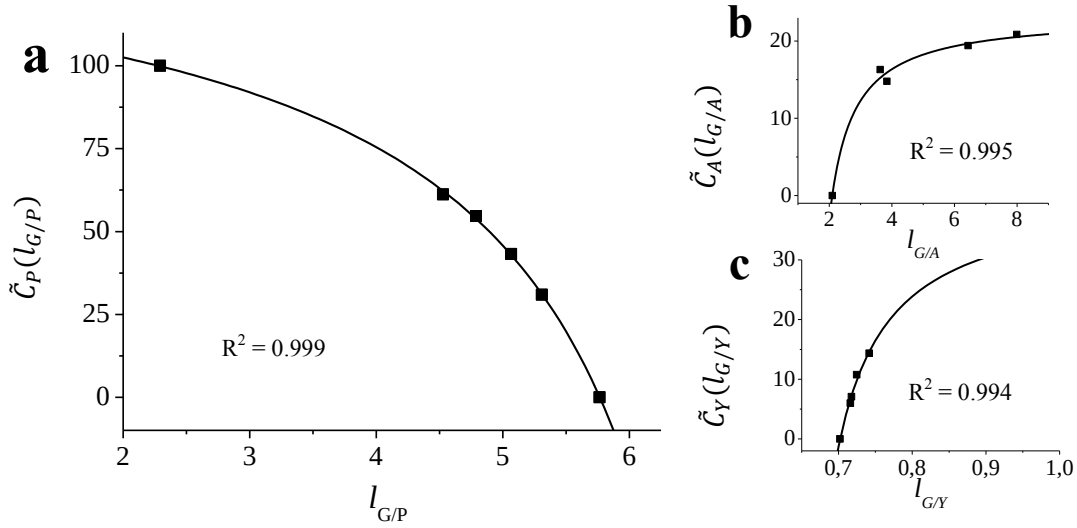

Figure 2. Calibration curves for determining the ratio of Nd^{3+}:YAG main phase to the impurity phases: a - Nd^{3+}:YAP, b - γ-Al_2O_3, c - Nd^{3+}:Y_2O_3

The same coefficients $l_{G/A}$ and $l_{G/Y}$ were calculated for the ratios Nd^{3+}:YAG/ Al_2O_3 and Nd^{3+}:YAG/Nd^{3+}:Y_2O_3 respectively. Unlike (2), in these cases the intensity ratio was used instead of the light sums ratio, as the spectrum ranges featuring the luminescence of only two phases appeared to be short. For parameter $l_{G/A}$ the ratio of intensities at wavelengths 577.0 nm and 688.0 nm was used. For $l_{G/Y}$ – the ratio of intensities at 938.7 nm and 945.8 nm. The resulting calibration curves $\tilde{C}_A(l_{G/A})$ and $\tilde{C}_Y(l_{G/Y})$ are resented in Fig. 2 b,c.

To find the initial concentration of all the phases C_G, C_P, C_Y and C_A the obtained values $\tilde{C}_P(l_{G/P})$, $\tilde{C}_A(l_{G/A})$, $\tilde{C}_Y(l_{G/Y})$ should be put into (1).

Table 3 shows the percentage of concentrations of all phases according to X-ray phase analysis and the luminescent method (LM) for the multiphase ceramics, which was described above. The table shows that the found values proved to be close, but the present difference is associated with not taking into consideration $Y_4Al_2O_9$ phase. When it is necessary to solve a problem of phase composition identification, including this structure, one has to create the corresponding standard samples where its concentration is enough to build a calibration curve.

Table 3. The composition of multiphase samples according to X-ray phase analysis and LM

	Ceramics no. 1		Ceramics no. 2		Ceramics no. 3		Ceramics no. 4	
	X-ray, %	LM, %	X-ray, %	LM, %	X-ray, %	LM, %	X-ray, %	LM, %
Nd^{3+}:YAG	56.5	56.6	48.6	47.9	33.4	33.2	39.0	40.8
Nd^{3+}:YAP	25.3	25.6	37.0	36.0	52.7	54.8	47.0	47.5
Al_2O_3	13.6	13.9	12.8	12.4	5.8	6.3	7.6	7.3
Nd^{3+}:Y_2O_3	3.6	4.0	3.7	3.7	5.6	5.7	4.7	4.4
Nd^{3+}:$Y_4Al_2O_9$	1	-	1	-	2.5	-	1.7	-

Thus, using the example of Nd^{3+}:Y_2O_3-Al_2O_3 multiphase system, the possibility of rapid determination of the qualitative phase composition with the luminescent method is demonstrated, involving the building of calibration curves and featuring the use of standard samples.

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